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THERMOGRAVIMETRIC ANALYSIS (TGA) OF VARIOUS EPOXY COMPOSITE FORMULATIONS

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14. ABSTRACT
Determined the thermal decomposition process of epoxy samples developed by the Florida Agriculture and Mechanical University/Florida State University (FAMU/FSU) Department of Engineering on SSG 3.0.6 containing a variety of additives including Polyhedral Oligomeric Sil Sesquioxanes (POSS) and Carbon Nanotubes. Thermogravimetric Analysis (TGA) was used to obtain data for decomposition in air. The data will be used to refine formulations of the additives incorporated into the epoxy.

15. SUBJECT TERMS

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MEMORANDUM FOR: Chuck Zhang
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FROM: Seymour Stern, Douglas Dierdorf
Air Force Research Laboratories/MLQD.

SUBJECT: Thermogravimetric Analysis (TGA) of Various Epoxy Composite Formulations.

1. BACKGROUND. Under SSG: 3.0.6 the Florida Agricultural and Mechanical/Florida State University (FAMU/FSU) Department of Engineering prepared 14 epoxy composite samples containing a variety of additives including Polyhedral Oligomeric Sil Sesquioxanes (POSS), Multiwall Carbon nanotubes (MWCNT) and Carbon Nanotubes (CN). These samples were submitted to the Fire Research Laboratory for evaluation by a variety of thermal analysis techniques. This report covers the TGA results**.**

2. OBJECTIVES. The objectives of this test were to determine the thermal decomposition process of various formulations as they burned in an air rich environment.

3. TEST EQUIPMENT DESCRIPTION. A Netzsch Simultaneous Thermal Analysis Apparatus, model number STA 409 PC was used. The instrument allows for the controlled heating of materials while measuring a variety of associated thermal properties. For this experiment, the system was used in the Thermogravimetric Analysis (TGA) mode. This instrument allows for sample sizes up to about 3 cc in volume to be tested.

4. SAMPLE DESCRIPTION. Samples were received as four inch squares, 1/8" thick plaques.

5. TEST PROCEDURES. Fourteen samples representing various compositions of Epon 862 and various additives were analyzed by Thermogravimetric Analysis (TGA) using the Netzsch STA 409 PC unit. Samples were cut from the plaque and each ranged in weight from 75 to 160 mg. TheTGA unit was programmed to control from 30C to 1150C increasing at 5C/minute under an air flow of 50 cc/min. This flow is sufficient at the aforementioned ramp rate to assure complete combustion at each stage. As the samples were unfamiliar to this lab, a default range up to 1150C was used so as not to miss any changes. Based upon the results observed, an upper limit of 800C would be more than adequate. Frequently a ramp of 10C/minute is used. Because of the subtle differences in formulations, a lesser ramp was used so as not to compress and hide these differences.

Analyses were performed and reported in the same order as in the table submitted with the samples (See Appendix). This table had four subunits representing the different formulation schemes used at FSU. For each subunit, one or two variables (MWCNT, POSS, and CN Fiber) were changed in the formulation of each composite plaque in that subunit. The results are presented as follows: For each subunit, a chart showing all components of that group on one graph, followed by individual graphs of weight changes vs. temperature. Percent weight changes were determined by using Netzsch Proteus Software, Version 4.3.

6. TGA RESULTS OF FSU SUBMISSION of 14 EPOXY COMPOSITE SAMPLES AND DISCUSSION

Two factors went in to deciding where to set temperature ranges for weight changes. The first issue is volatiles, including water and possibly residual solvents. It was observed that three hundred degrees Celsius gave consistent results in the samples submitted at levels one would expect (1-2%).

As all the submitted samples had a curve with a gradual change of slope in the region of 450C to 480C, the first derivative curve was employed to more precisely determine the inflection point. As will be noted, there are differences in the values between samples. If the three mass changes listed are summed, the values will be slightly less than 100%, the difference being the residual mass.

Sample #	% Mass loss change 30^{o}C to 300^{o}C	% Mass loss from 300^{o}C to first inflection	First inflection point (^{o}C)	Second inflection point (^{o}C)	% Mass loss from first to second inflection points
1	1.62	62.92	468	645	35.45
2	1.39	66.41	468	645	31.98
3	1.34	64.54	485	670	33.94
5	1.13	64.55	476	670	33.71
8	1.46	66.34	487	673	31.66
9	1.41	64.62	480	660	33.11
11	1.07	66.68	495	692	30.89
13	1.41	61.11	485	670	35.12
79	1.44	61.45	468	646	36.32
80	1.46	62.88	477	655	34.44
82	1.36	61.9	458	663	35.33
85	1.55	60.87	460	660	36.89
86	1.38	55.72	460	685	41.3
87	1.86	59.38	469	698	37.42

Table 1

For each of the 14 samples, a portion was analyzed from a corner of each plaque. While TGA results on identical materials are quite precise and reproducible, the variability in a given sample due to the formation of the plaque in the molding process is unknown. To this end, sample 86 was arbitrarily chosen as a proxy for all samples. It was analyzed an additional four times, with portions taken at random throughout the plaque. Because of resource constraints, just sample 86 was analyzed for variability. As will be seen the numbers do vary, both in terms of relative percentages and in terms of temperature cut offs. It is expected that similar results would be obtained with the other samples.

Including the initial sampling of the edge from 86, five sets of data were available. The statistical results are as follows:

Trial #	% Mass loss change 30°C to 300°C	% Mass loss change 300°C to first inflection	Temperature of first inflection (°C)
edge	1.38	55.72	460
1	2.26	59.56	466
2	1.93	63.43	478
3	1.62	62.62	477
4	2.07	60.51	473
Average	1.852	61.40	470.8
Std Deviation	0.352	1.59	7.66

Table 2

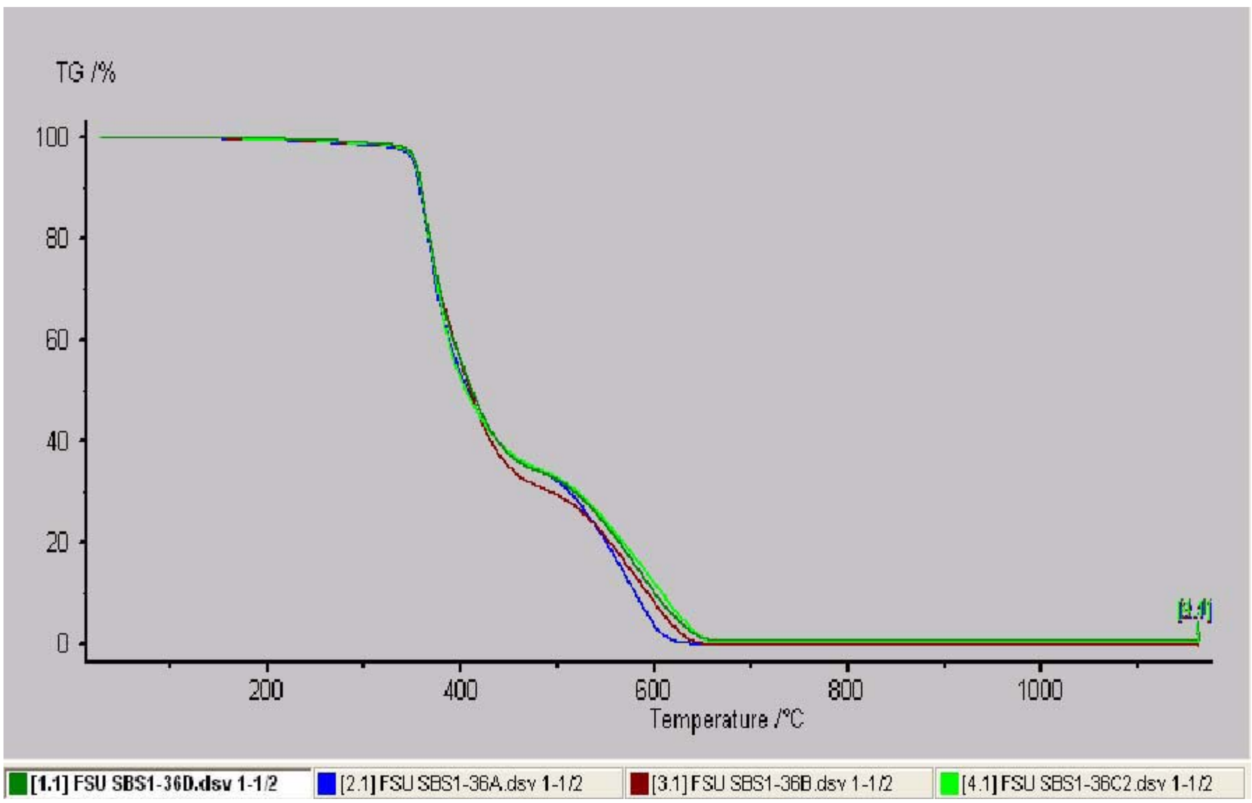
Thus when you look at the single value results for the companion pieces, 85 and 87, below, it is not certain that the apparent differences might fall within the range of sample inhomogeneity. Sample 85 is used for comparison purposes as it is part of the same subset of parts submitted, and therefore contains similar components.

Sample #	weight percent surface	300 to first inflection	Temperature of first inflection
85	1.55	60.87	460
87	1.86	59.38	469

Table 3

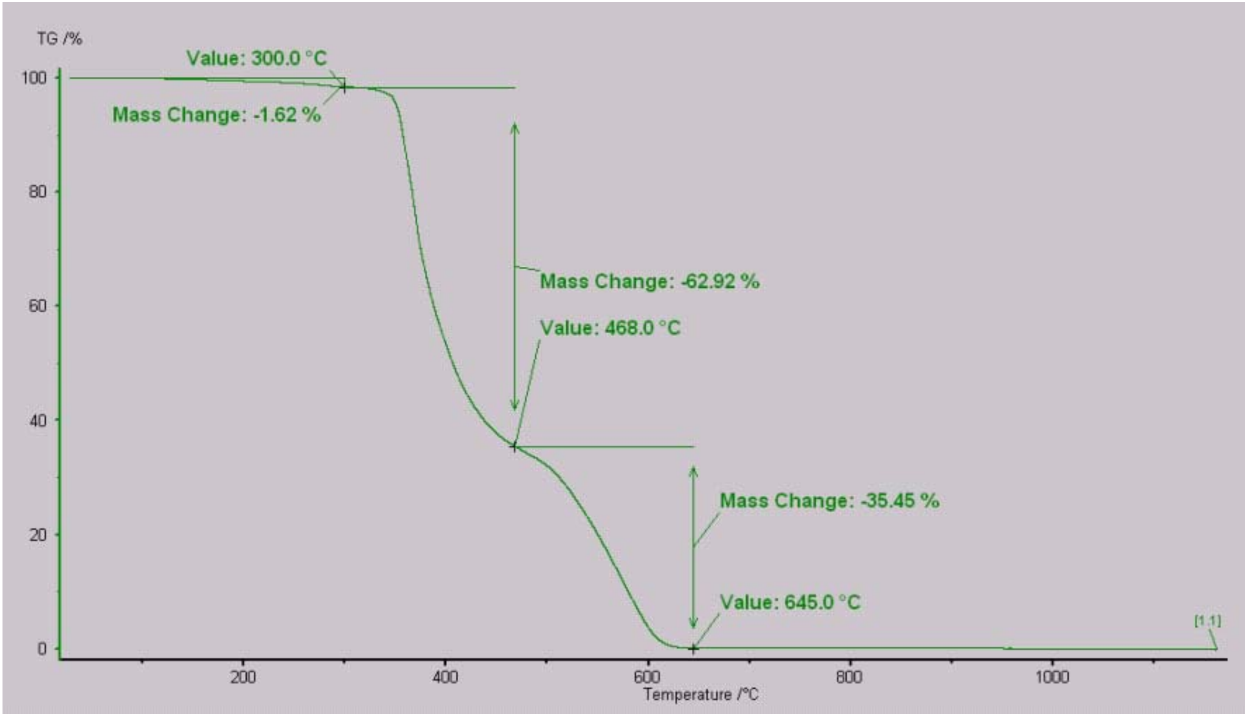
To resolve this issue properly would require significantly more analyses for each of the other 13 materials. No further TGA tests are planned unless justified by cone calorimetry data.

Thermograms follow. Three terms are abbreviated as follows: Multi Wall Carbon Nanotubes (MWCNT), Polyhedral Oligomeric Sil Sesquioxanes (POSS) and Carbon Nanotubes (CN). The subunits represent different formulation trials with one or more of the additives. For each subunit, a composite overlay of each thermogram is presented, followed by the separate thermogram for each sample.

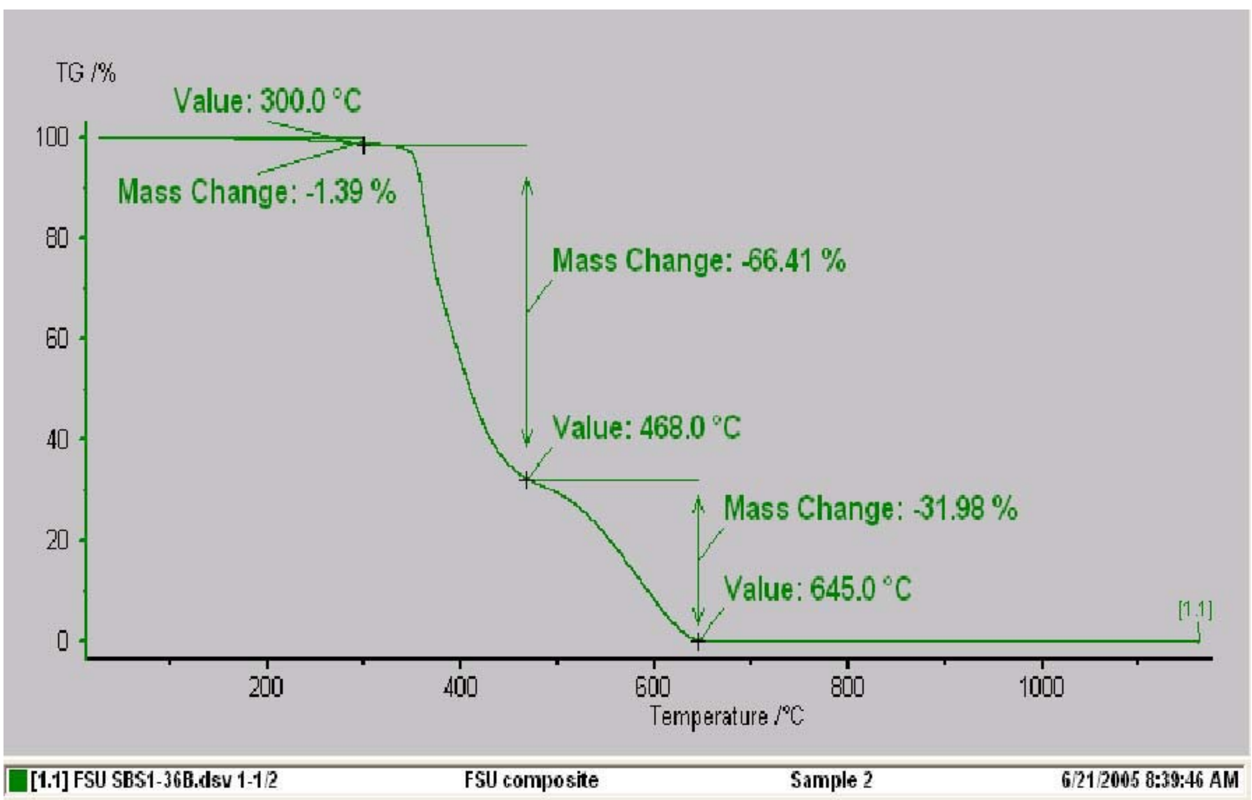


Samples 1, 2, 3, 5
1 2 3 5

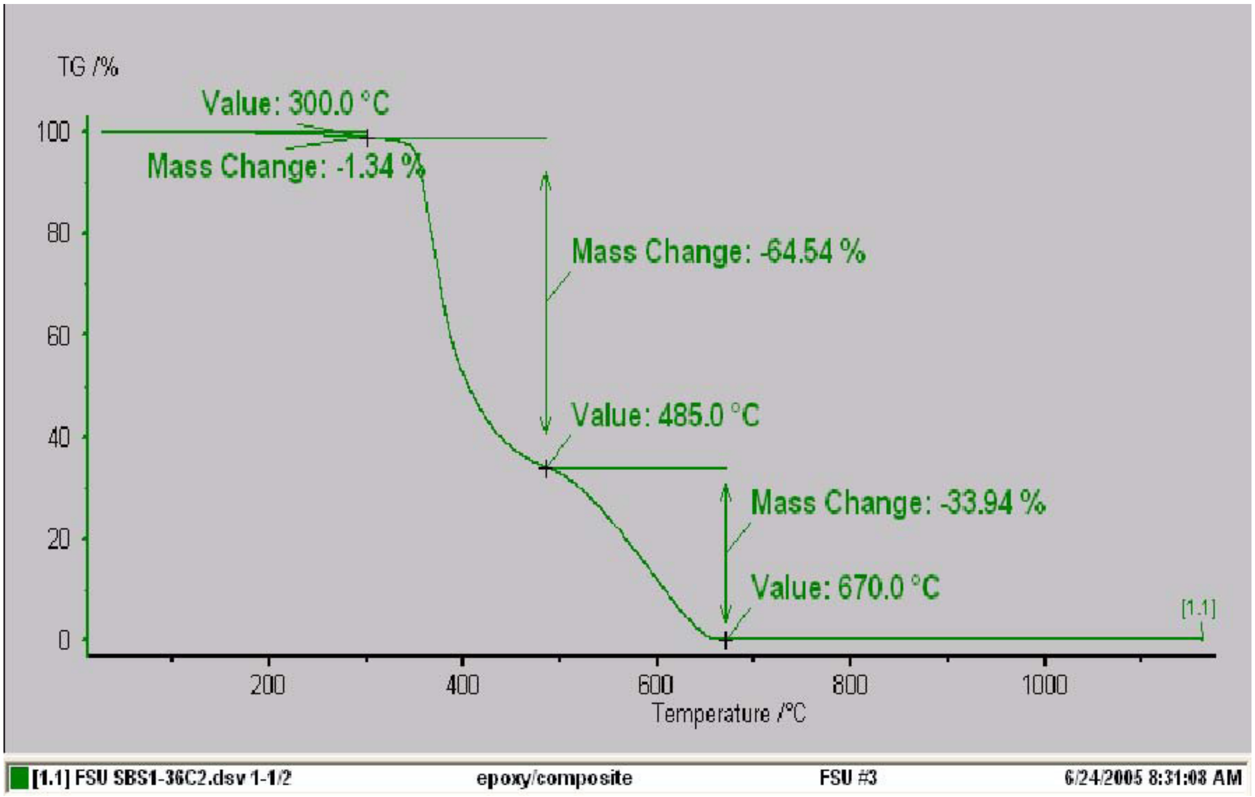
Sample #	MWCNT	POSS	CN Fiber
1	0	0	0
2	0.5		
3	1		
5	2		



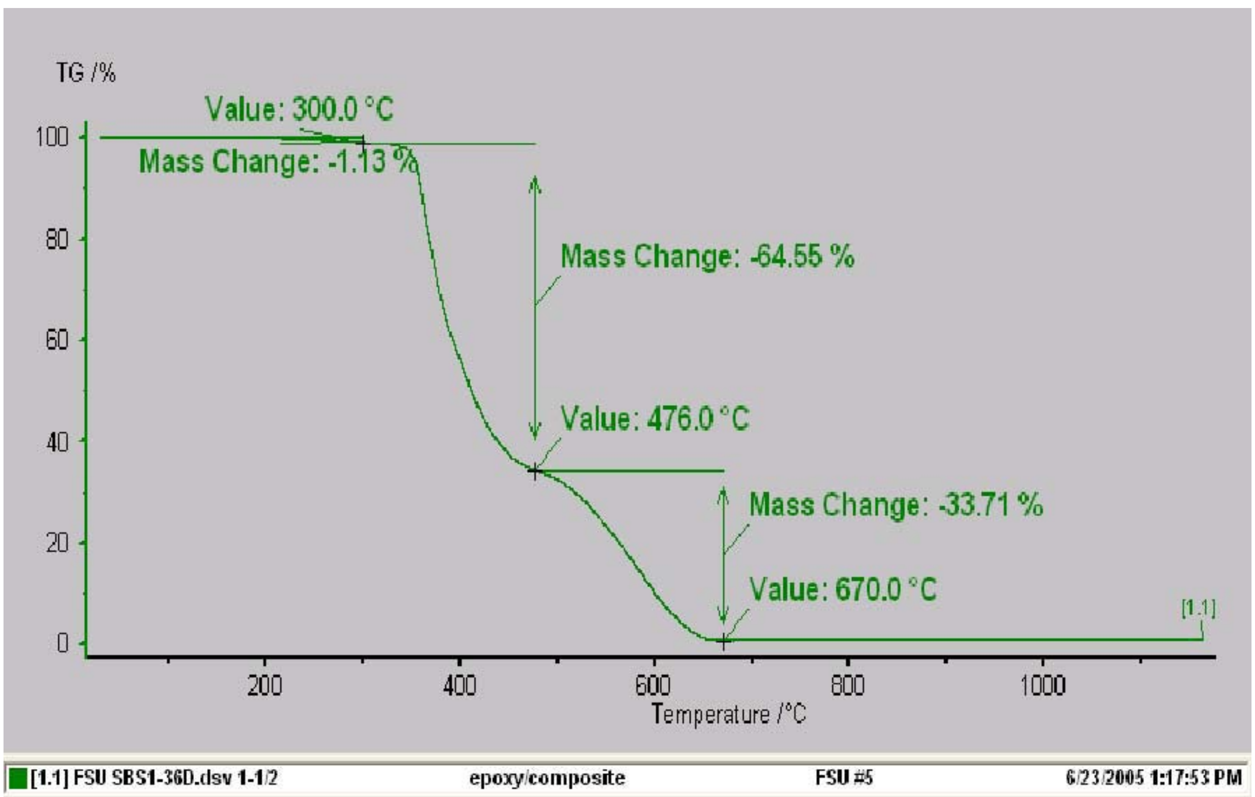
Sample #1



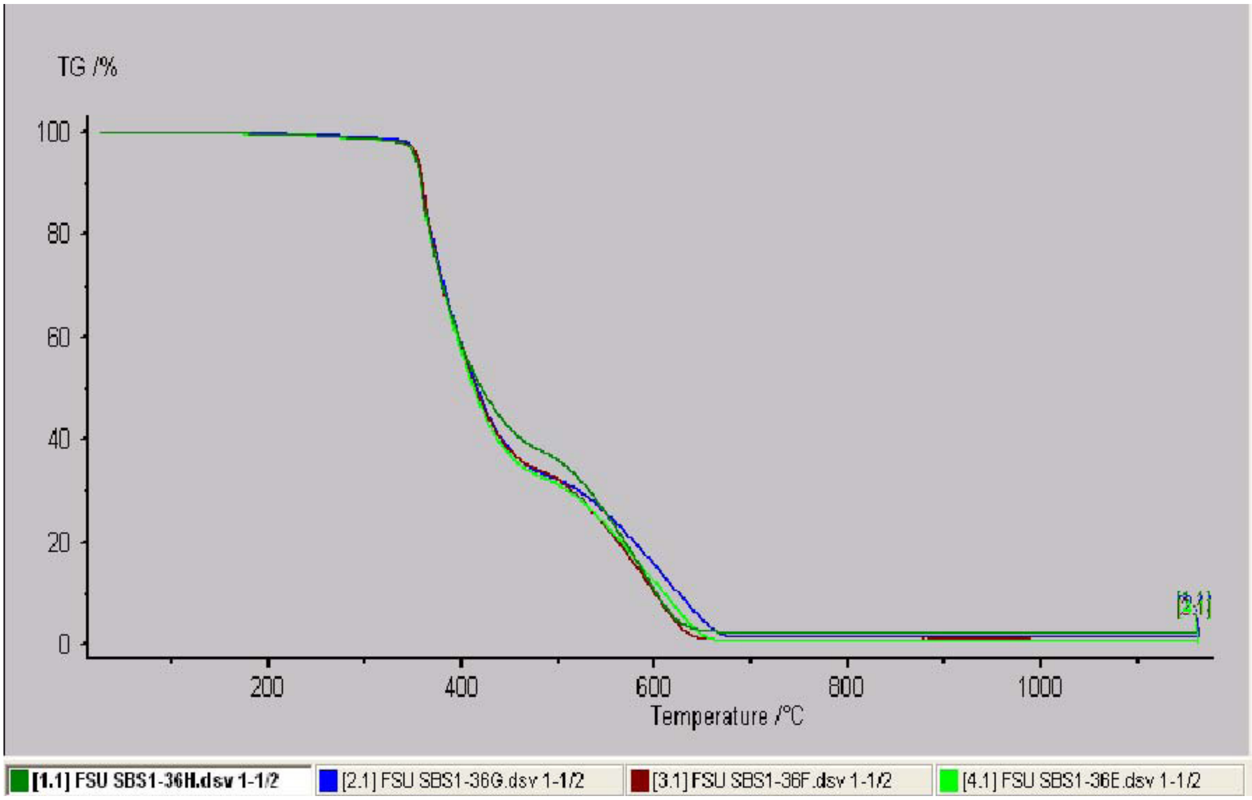
Sample #2



Sample #3

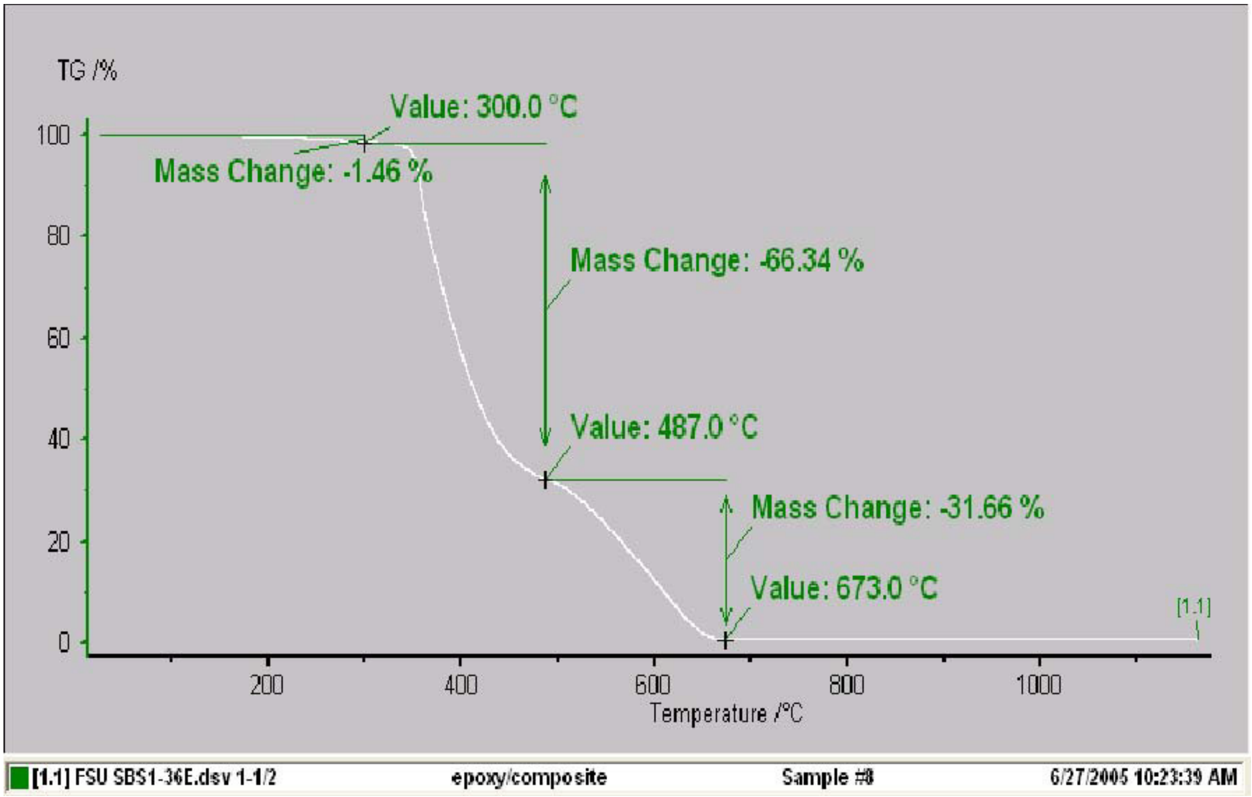


Sample #5

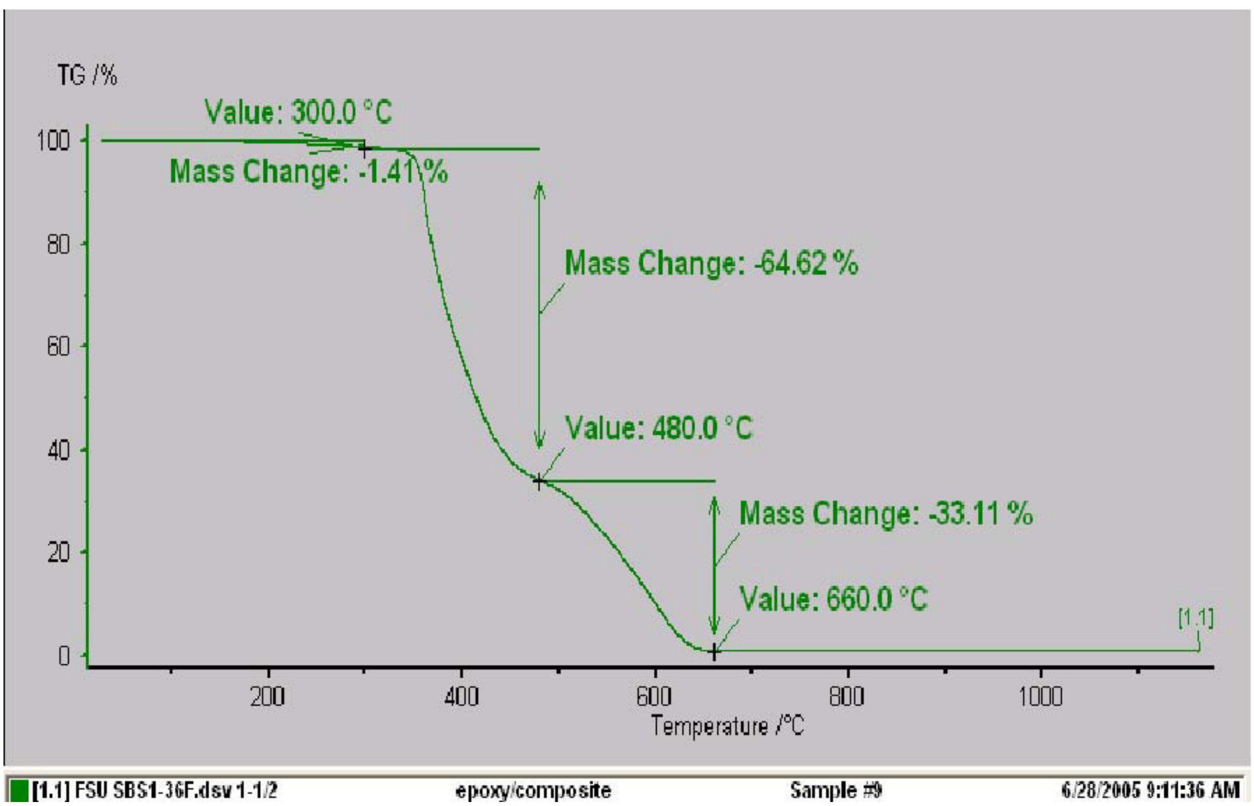


Samples 8, 9, 11, 13
8 9 11 13

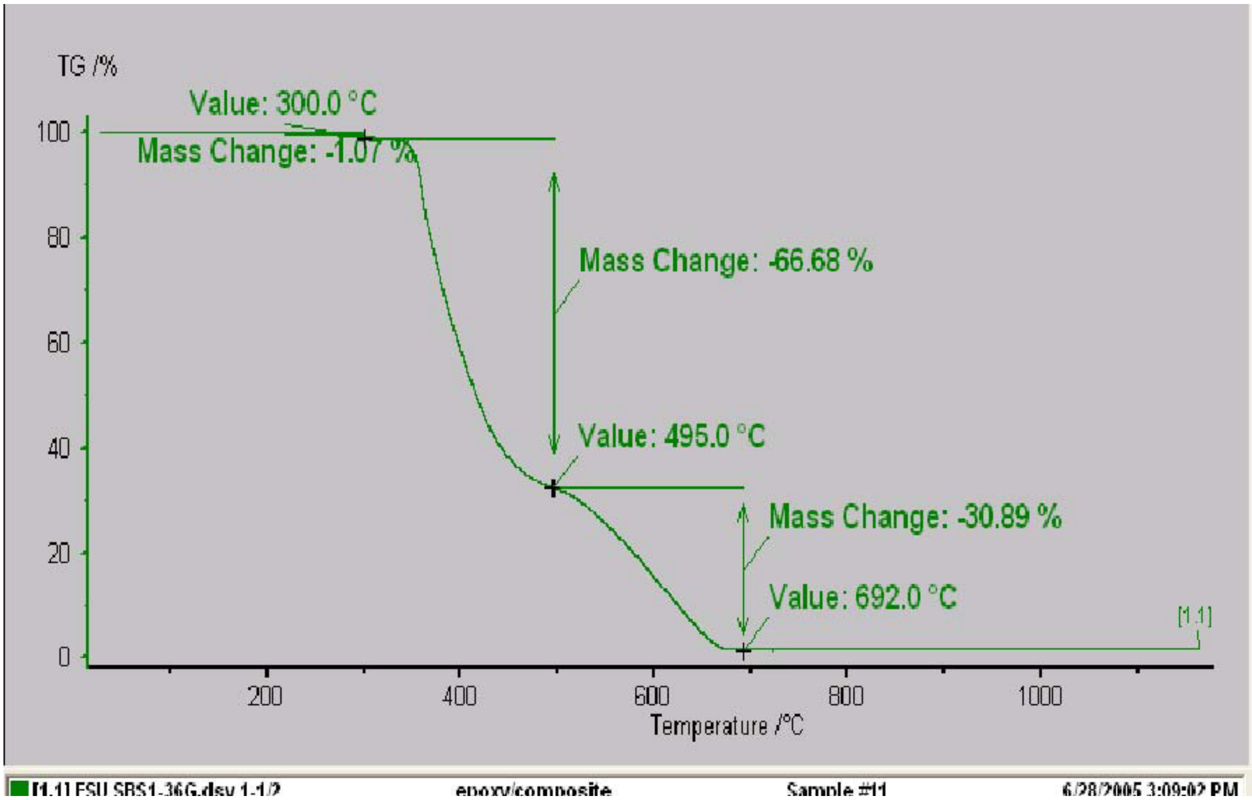
Sample #	MWCNT	POSS	CN Fiber
8		0.5	
9		1	
11		2	
13		5	



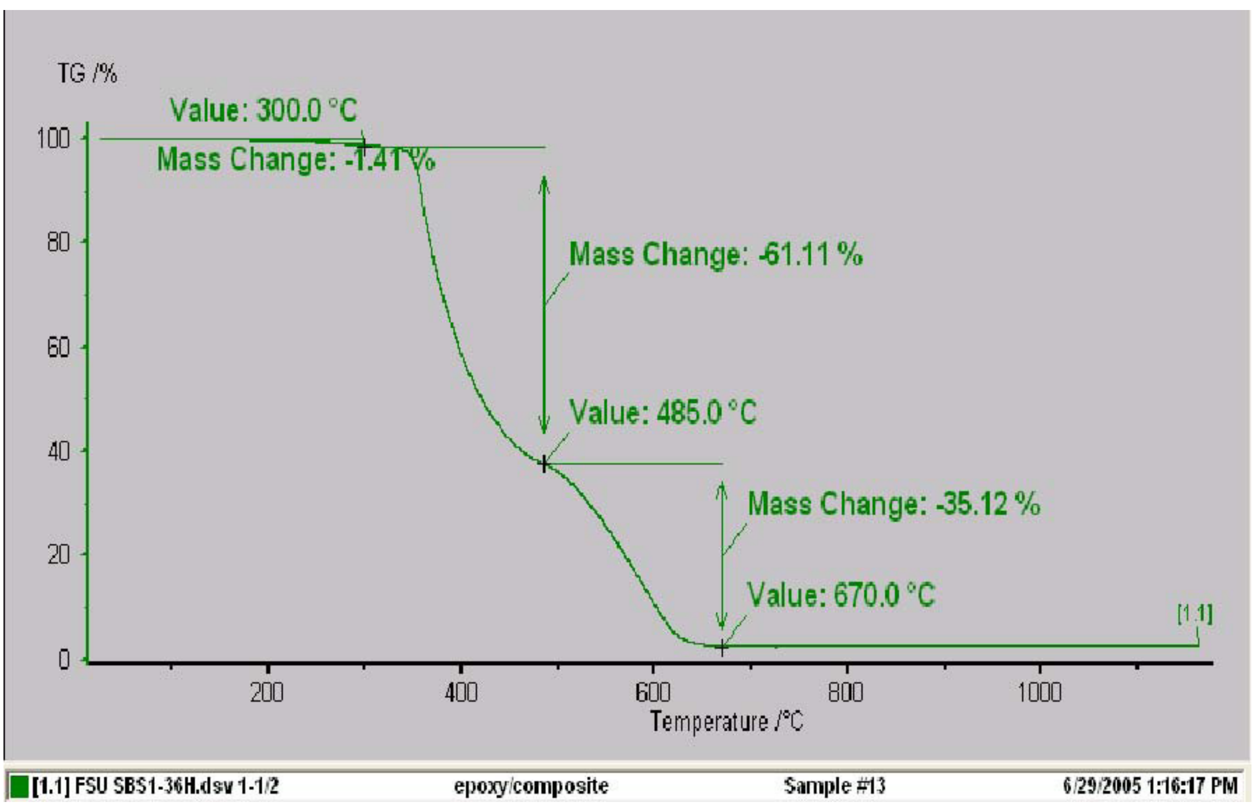
Sample 8



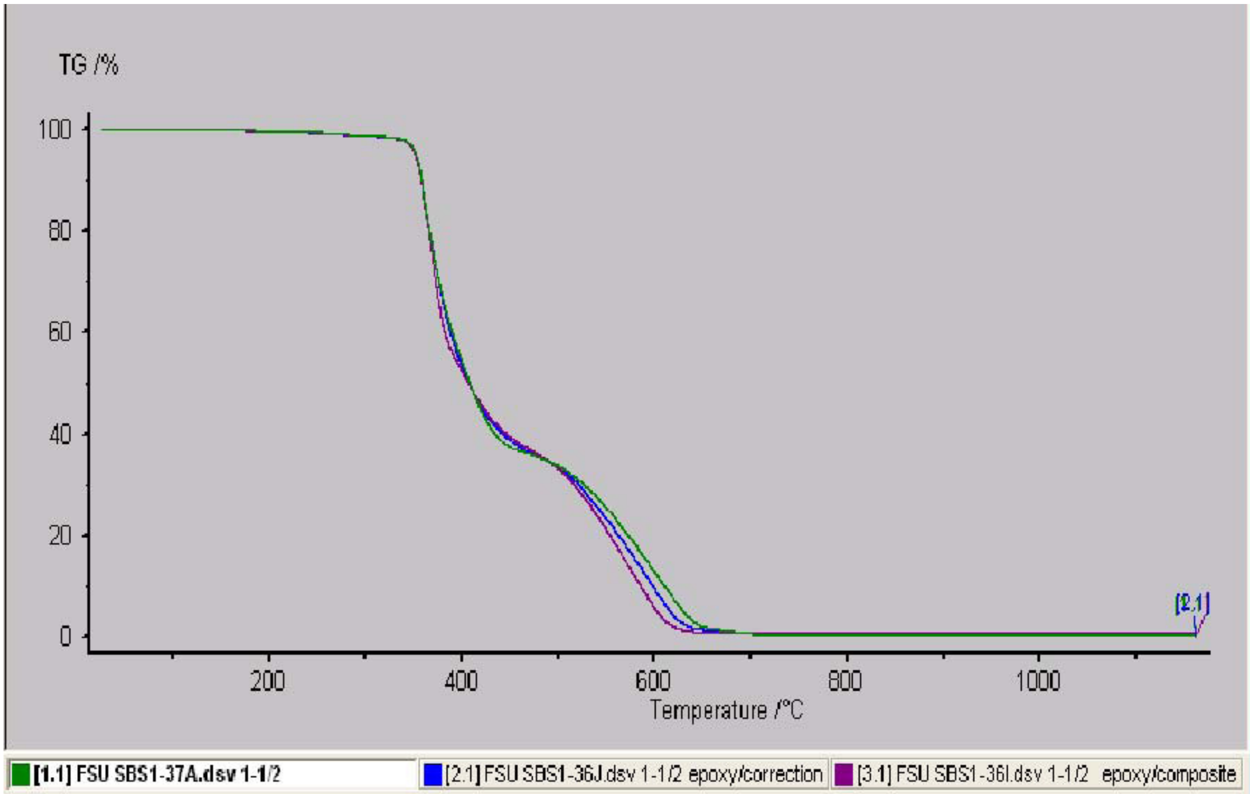
Sample #9



Sample #11

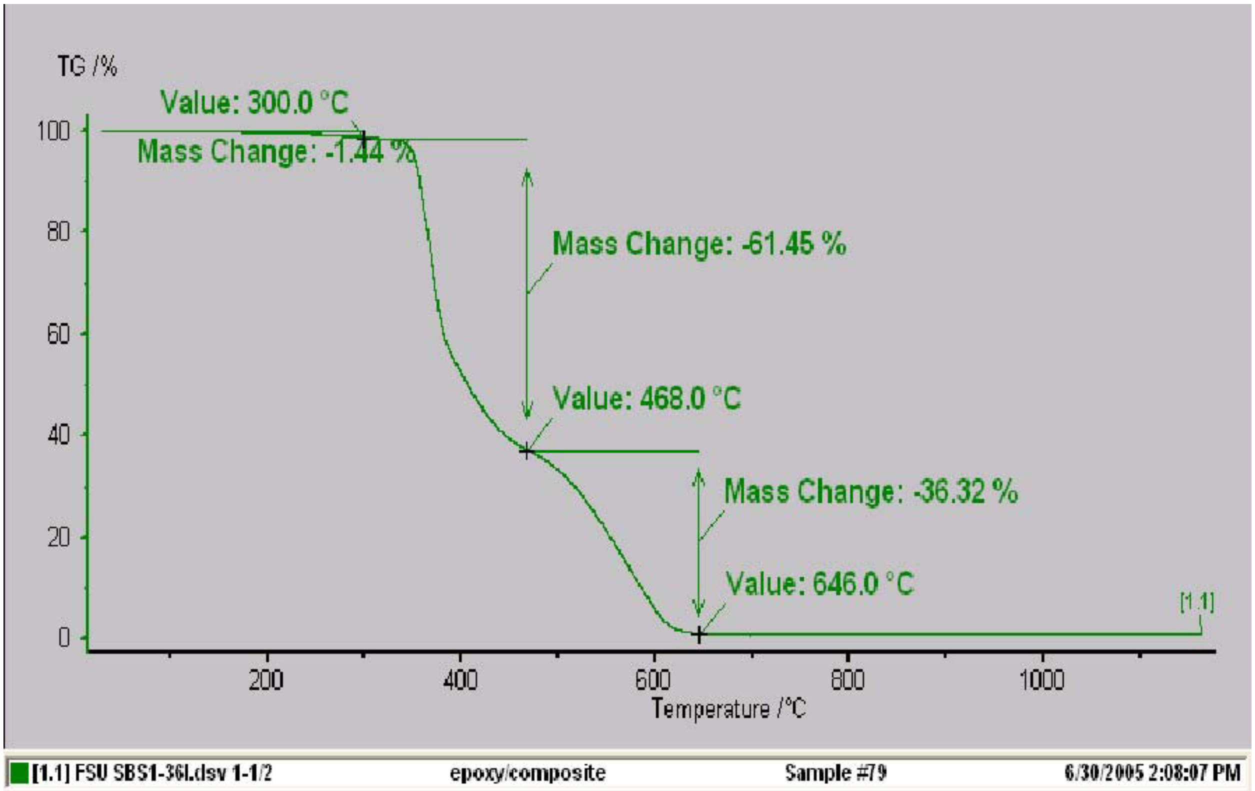


Sample #13

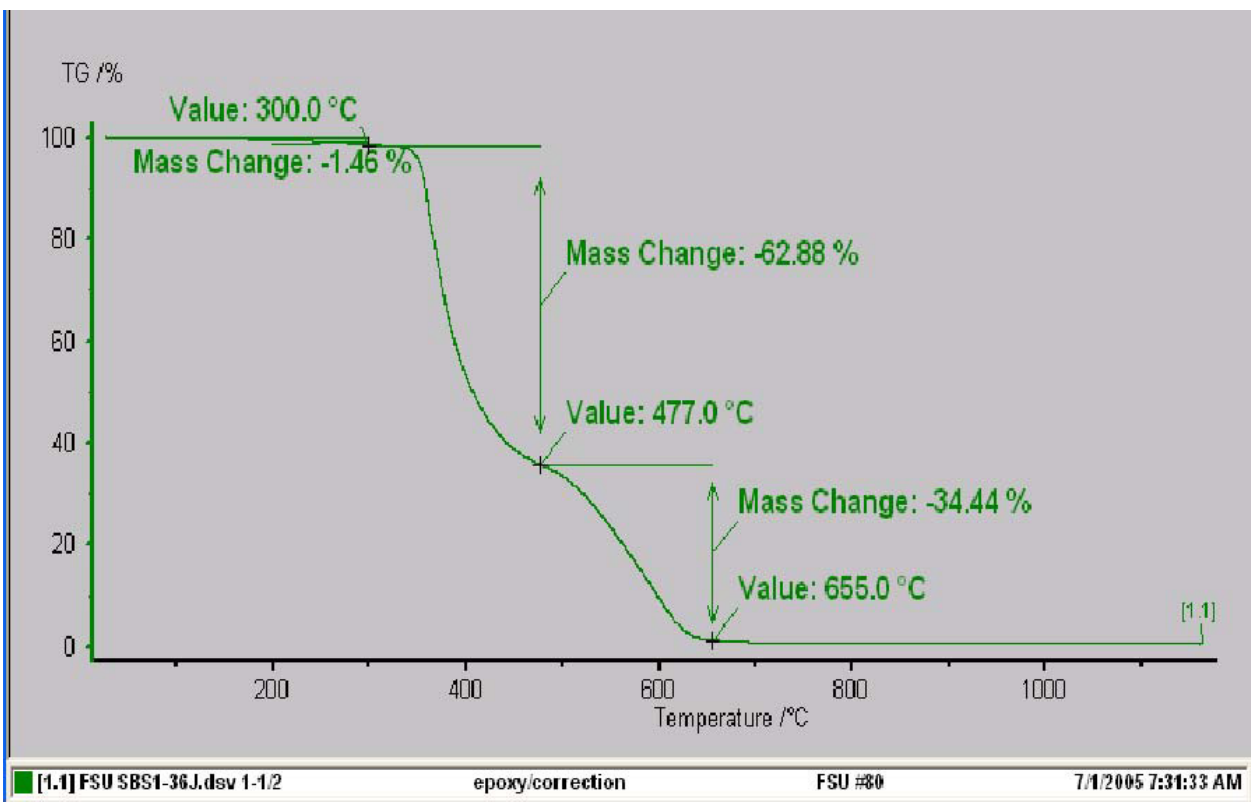


Samples 79, 80, 82
79 80 82

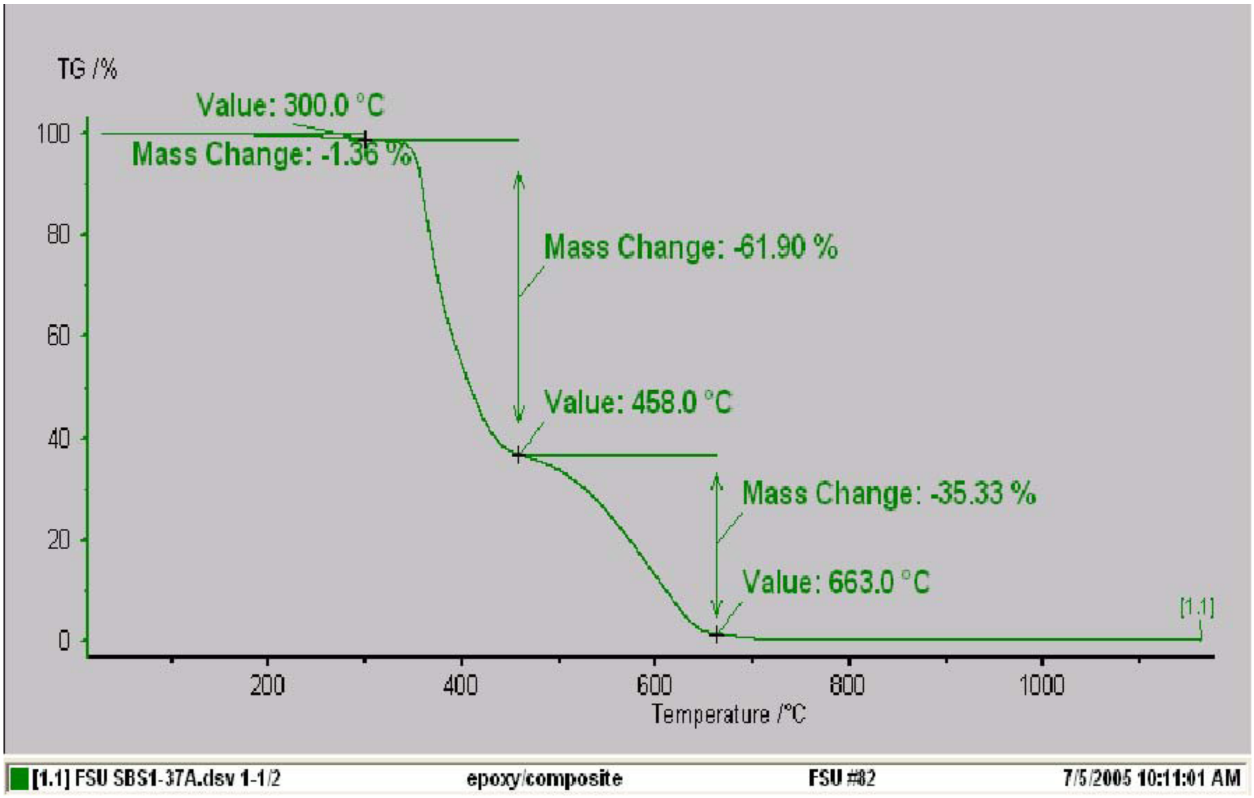
Sample #	MWCNT	POSS	CN Fiber
79			0.5
80			1
82			2



Sample #79

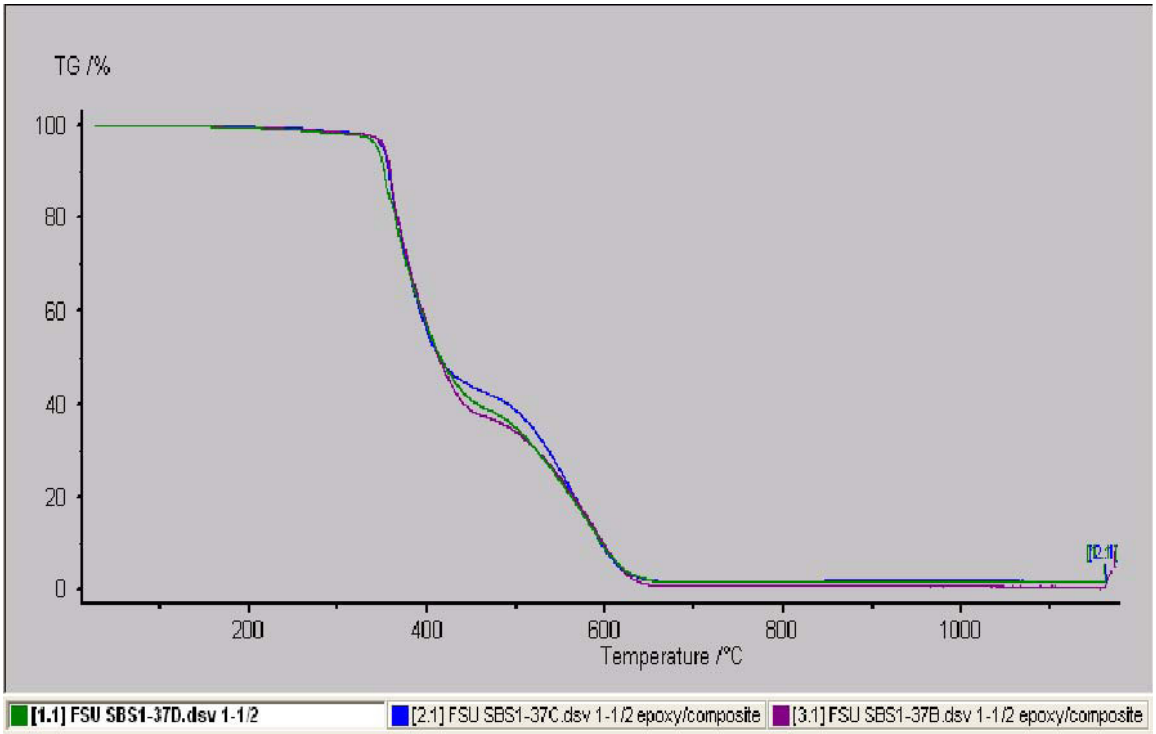


Sample #80



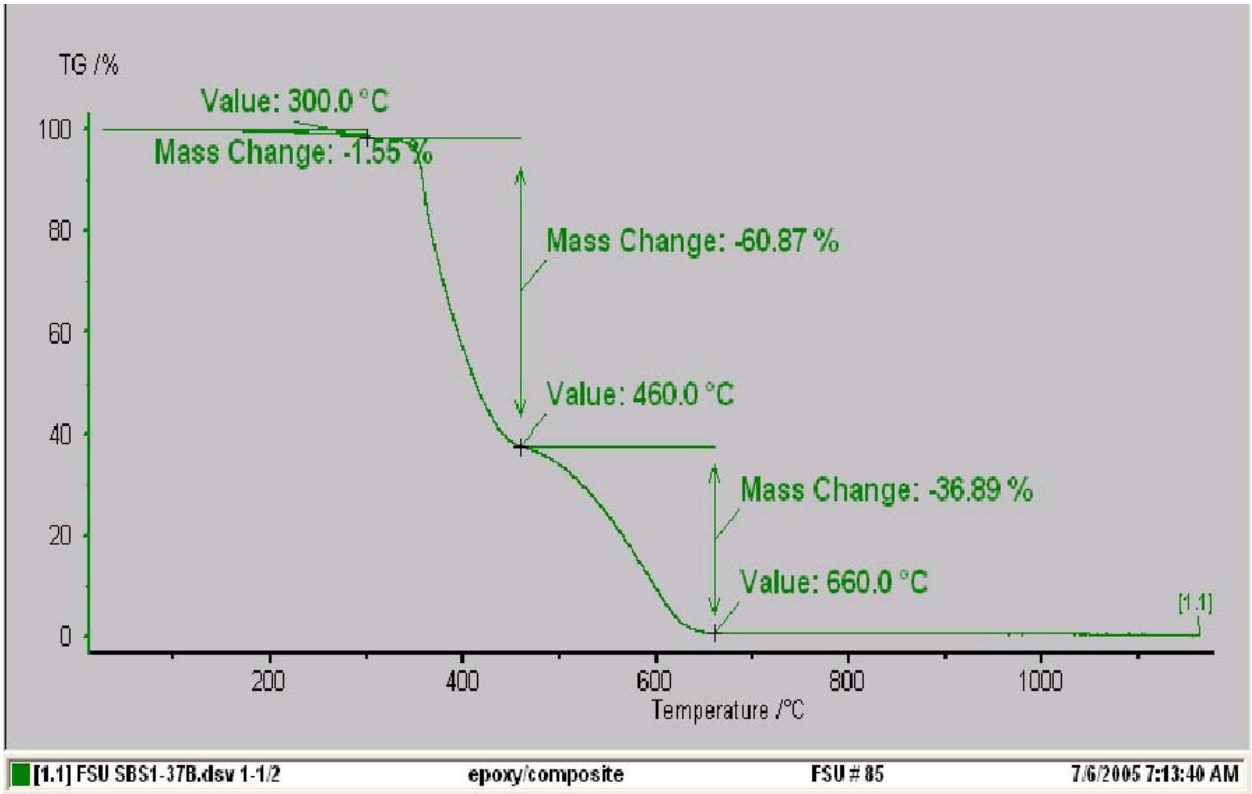
TG /%
Value: 300.0 °C
Mass Change: -1.36 %
Mass Change: -61.90 %
Value: 458.0 °C
Mass Change: -35.33 %
Value: 663.0 °C
[1.1]
100
80
60
40
20
0
200
400
600
800
1000
Temperature /°C
[1.1] FSU SBS1-37A.dsv 1-1/2
epoxy/composite
FSU #82
7/5/2005 10:11:01 AM

Sample #82

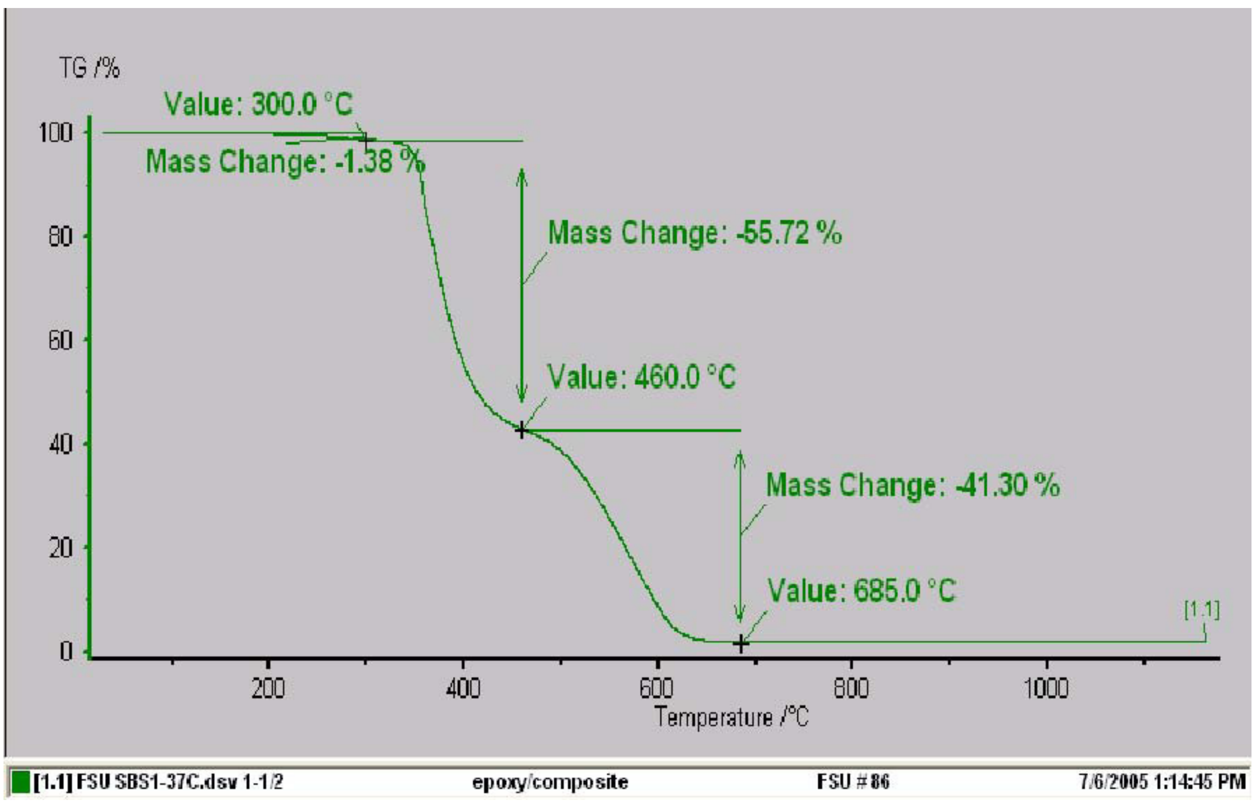


Samples 85, 86, 87
85 86 87

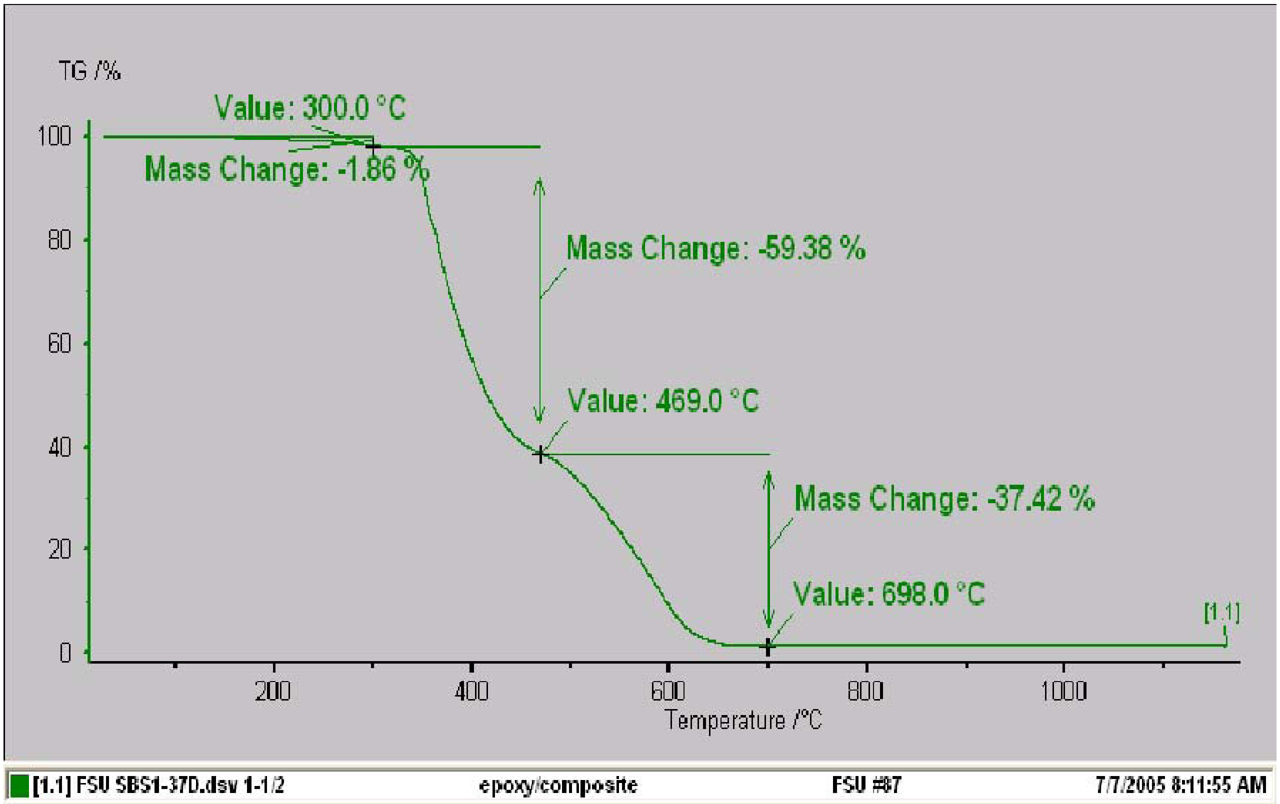
Sample #	MWCNT	POSS	CN Fiber
85	0.5	0.5	
86	1	1	
87	2	2	



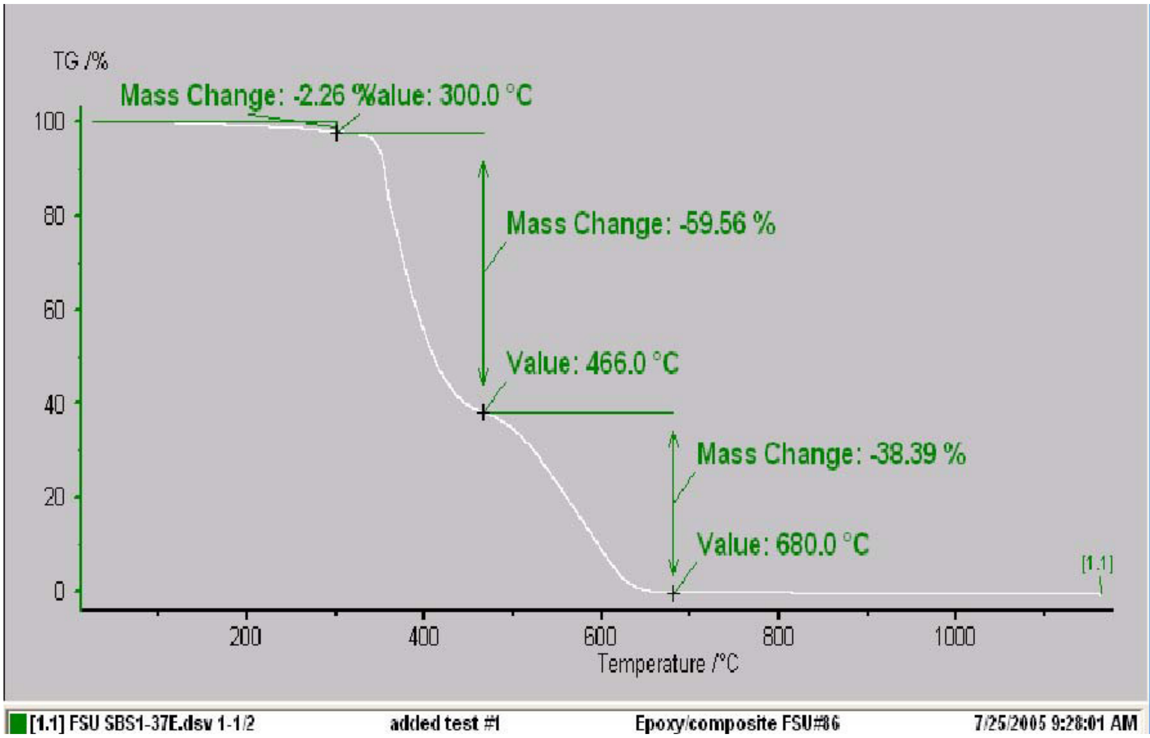
Sample #85



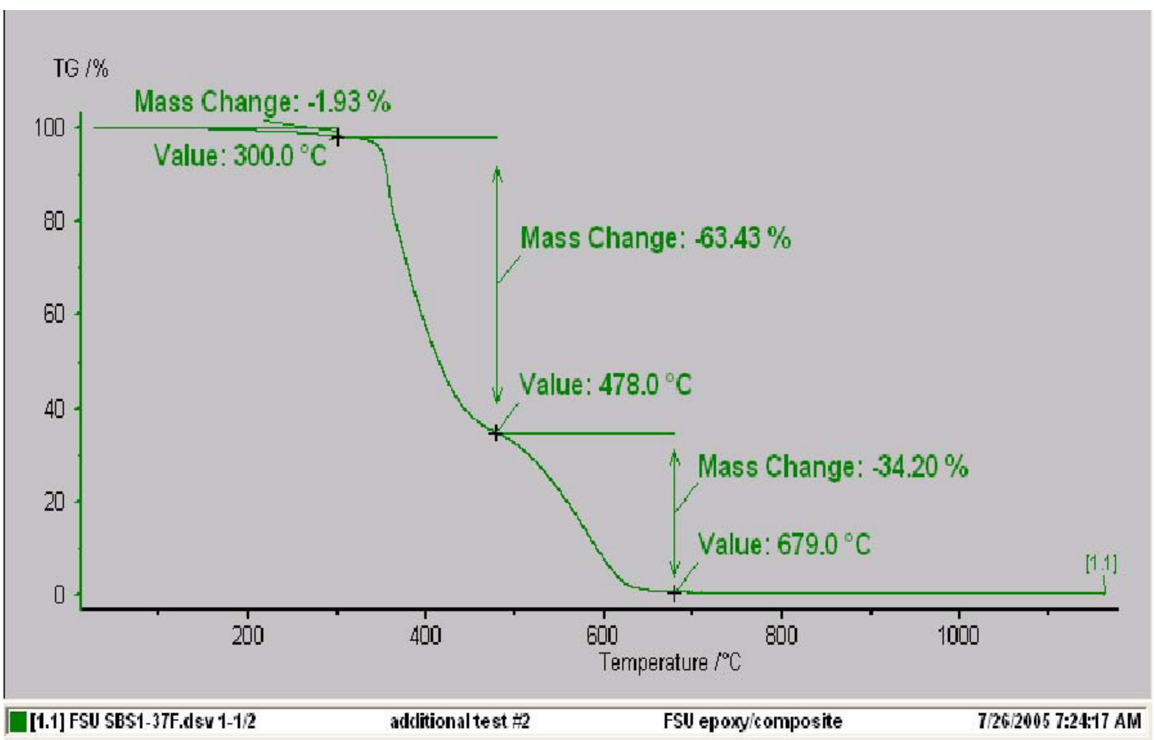
Sample #86


TG /%
Value: 300.0 °C
Mass Change: -1.86 %
Mass Change: -59.38 %
Value: 469.0 °C
Mass Change: -37.42 %
Value: 698.0 °C
[1.1]
100
80
60
40
20
0
200
400
600
800
1000
Temperature /°C
[1.1] FSU SBS1-37D.dsv 1-1/2
epoxy/composite
FSU #87
7/7/2005 8:11:55 AM

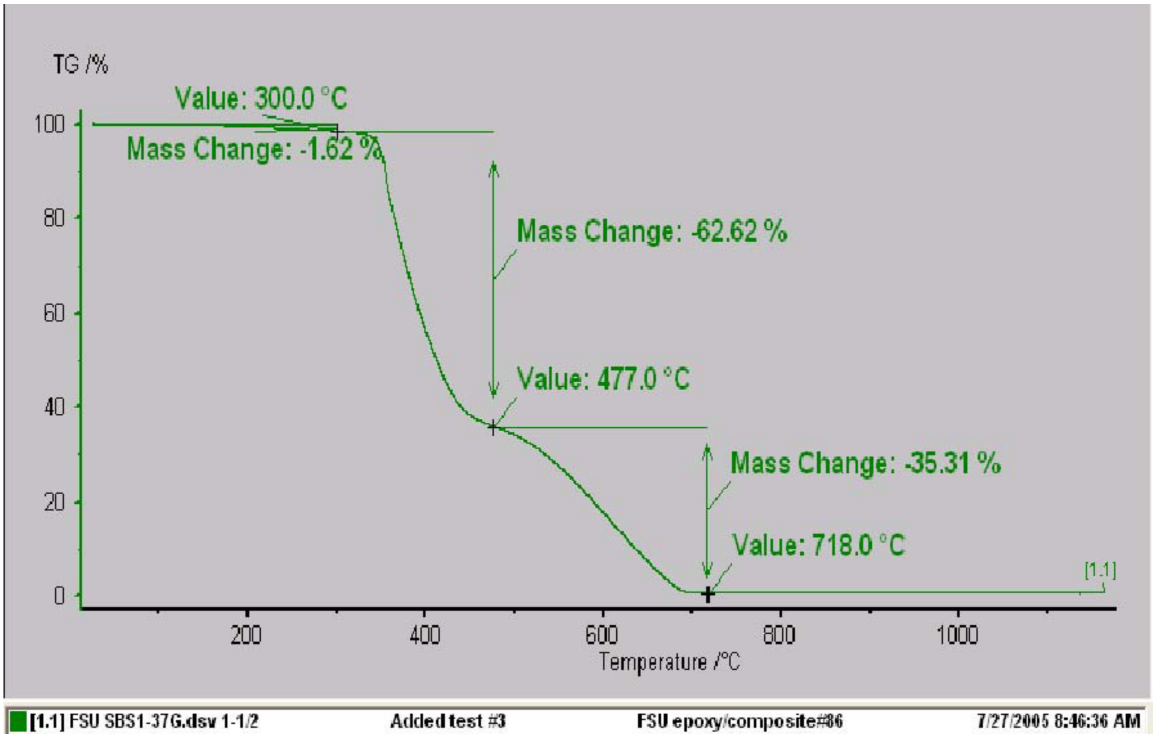
Sample #87



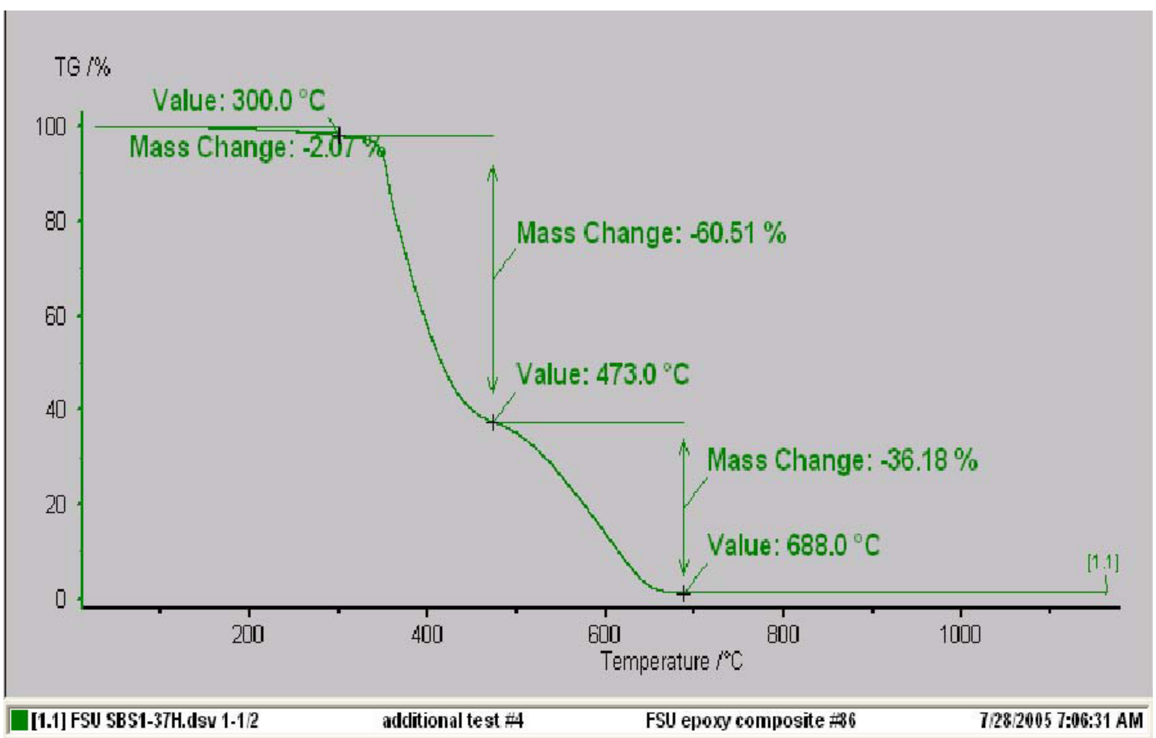
Variability test #1, Sample 86



Variability test #2, Sample 86



Variability test #3, Sample 86



Variability test #4, Sample 86

APPENDIX

Sample #	MWCNT	POSS	CN Fiber
1	0	0	0
2	0.5		
3	1		
5	2		
Sample #	MWCNT	POSS	CN Fiber
8		0.5	
9		1	
11		2	
13		5	
Sample #	MWCNT	POSS	CN Fiber
79			0.5
80			1
82			2
Sample #	MWCNT	POSS	CN Fiber
85	0.5	0.5	
86	1	1	
87	2	2	